# Next-Generation Anodes for Lithium-Ion Batteries Fundamental Studies of Si-C Model Systems

Robert Kostecki

Lawrence Berkeley National Laboratory

Berkeley, California 94720

2017 Annual Merit Review

June 5-9, 2017, Washington DC

Project ID# ES262

# Overview

## Timeline

- PI participates in the ABR Program since 1999
- First phase of this project started in Oct. 1, 2015 and ended in Jan. 30, 2017.
- Second phase of this project started in Oct. 1, 2016 and end in Sept. 30, 2019.

## Barriers Addressed

- Enable Si-based batteries that can meet the targets for high-energy Li-ion batteries for PHEV and EV applications.
  - Understand fundamental phenomena that control function and operation of Si-based anodes in Li-ion batteries
  - Provide guidance to rational design of Si-based anodes, including functional properties of advanced binders

## Budget

- FY17 funding $800K
- FY16 funding $400K

## Partners

- ANL
- LBNL/ALS
- NREL
- ORNL
- SNL

# Relevance : Objectives

1. Tackle the barriers associated with development of an advance lithium ion negative electrode based upon intermetallic Li-alloys active material
   - baseline model systems include Si, Ge, Sn, $SiO_x$ and their alloys, advanced binders (e.g., polysiloxane, conductive polypyrene and polyacrylic) and conductive additives such as graphite and carbon black
2. Understand and eliminate fundamental scientific and technical limitations to implementation of a silicon based anode in commercial cells
   - address the inherent non-passivating behavior of silicon and intermetallic electrodes in organic electrolytes, which results in large irreversible capacity loss and gradual electrolyte consumption during the electrode operation.
3. A better understanding of the underlying principles that govern these phenomena is inextricably linked with successful implementation of high energy density materials such as Si in Li-ion cells for PHEVs and EVs.

# Milestones

1. Established protocols for sample synthesis, preparation, characterization and analysis to ensure compatibility of experimental data from all consortium members. Protocols will be posted on the shared cloud drive and provided to the ANL lead silicon electrode deep dive. **Status Completed (December, 2015)**
2. Complete round robin sample analysis to ensure protocols established in quarter 1 are functional. Results based upon less than 5% variance in electrochemical performance between laboratories to ensure equivalent starting materials and preparations. **Q2 status on schedule**
3. Define the relationship between the surface of the lithiated silicon and the nature of the SEI, by demonstrating that the chemical or physical properties are or are not affected by the nature of the silicon surface treatment; specifically by contamination, oxide content, dopant level, or degree of crystallinity. **Q3 status on schedule**
4. Go/No-Go: Determine if the nature of the silicon (purity level, doping and/or structure) have an effect on formation and evolution of the SEI. This will determined by observing measurable chemical and physical changes in the SEI layer between substrates. Criteria: Down selected the most promising model systems for future studies. **Q4 status on schedule**

# Diagnostic Evaluation of Model Si Anodes
## Approach

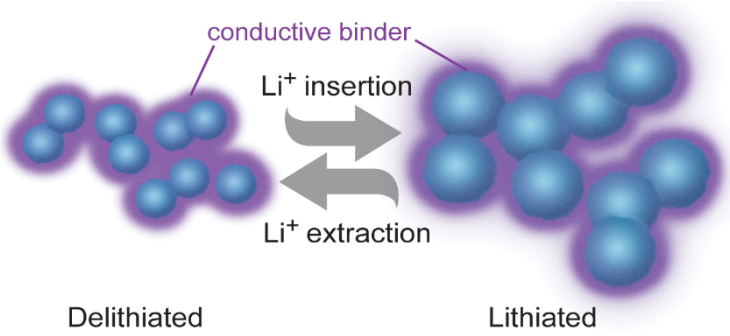
- Carry out rigorous diagnostic studies of Si and other intermetallic-based model electrodes to determine the key thermodynamic and kinetic parameters, which enable their function and operation in Li-ion batteries.

- Design model experimental systems to study basic processes, which include (1) concerted electron and ion transport at the electrode/electrolyte interface, and (2) spatial and temporal evolution of basic chemical building blocks and phase boundaries at the interface.

- Apply *in situ* and *ex situ* advanced spectroscopy/microscopy techniques such as far- and near-field optical techniques (FTIR, ATR-FTIR, IR aNSOM, Raman), scanning probe microscopy, spectroscopic ellipsometry and x-ray spectroscopy (XAS, XANES, EXAFS) to probe model Si model electrodes at an atom, molecular or nanoparticulate level.

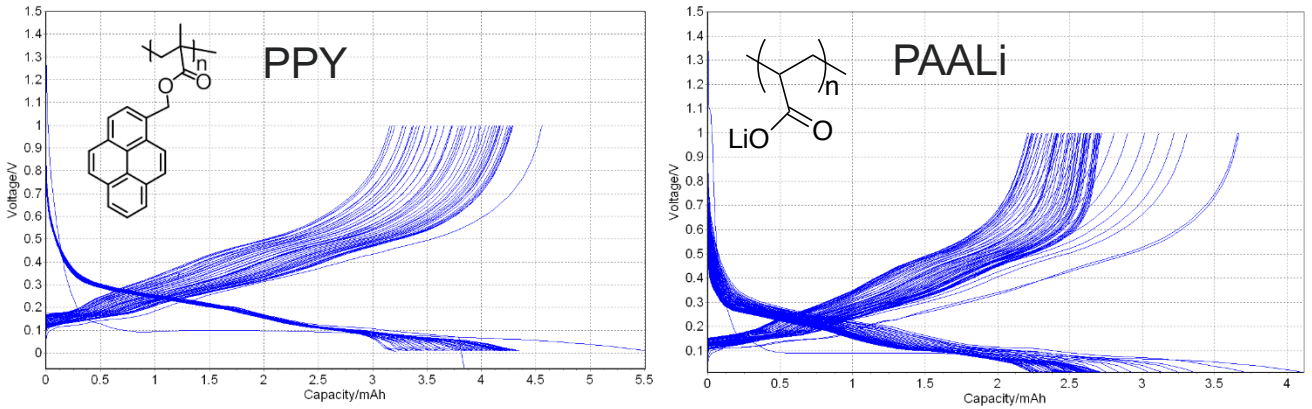
# Function and Operation of Advanced Binders in Si/C Anodes

Liu et al., *Adv. Mater. 2011, 23, 4679*




- Electronically and/or ionically conductive
- Chemically stable
- Good mechanical properties
- Compatible with electrode/cell manufacturing processes

15% Si, 73% graphite, 12% binder, 3 mg/cm$^2$ composite anode

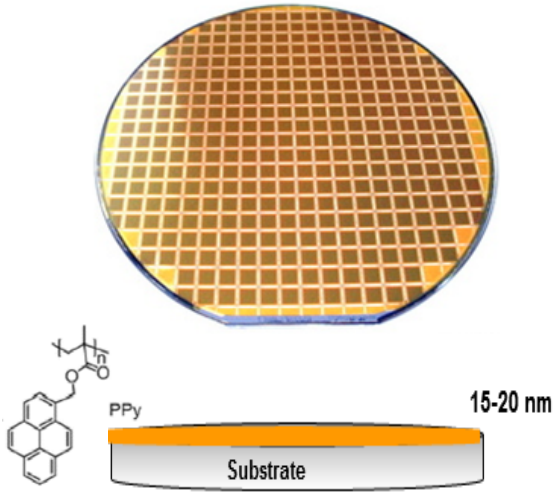



- Electrochemical performance of Si/C electrodes varies strongly with different binders.
- The rate and mechanism of the electrode degradation may depend on the binder properties.

*Thorough basic understanding of the binder modes of operation cannot be gained solely through testing commercial-type devices.*

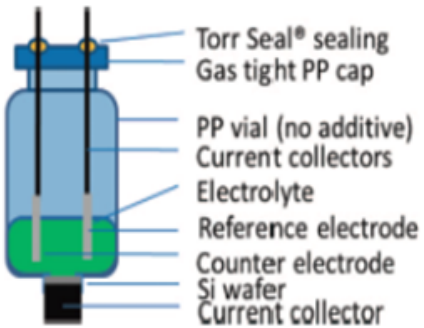
# Model Si/PPy Electrodes: Preparation and Testing

- Spin coat ~20 nm PPy thin-film on B-doped Si(100) wafers and Cu-coated (100 nm) Si wafer.
  - PPy raw polymer materials were supplied by Gao Liu (LBNL) and MERF (ANL)
  - Homogenous and pin-hole free PPy thin-film on Si wafer were produced.

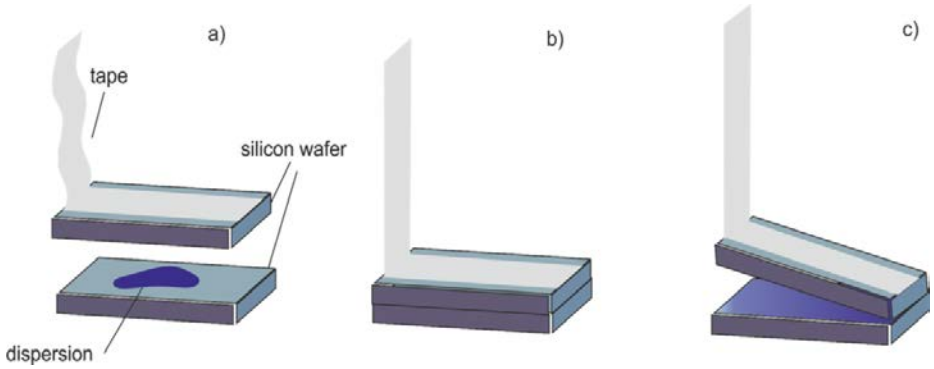



- Electrochemical measurements of model Si, Cu, Si/PPy, Cu/PPy electrodes in 1.2 M $LiPF_6$ EC:DEC 3:7 (wt%) 30 wt% FEC.
  - CV scan rate: 0.1 mV/s, potential range OCV ➔ 0.005 ➔➔ 2V

- Perform *ex situ* and *in situ* characterization studies to probe, monitor and evaluate interfacial properties of Si and Cu model electrodes.



# Mechanical Tests of PAA, Ppy and PVdF Binders




- *10 µL saturated solution of PPy or PVdF in NMP or PAALi in $H_2O$ squeezed between two pieces of Si or Si/Cu plates and dried.*
- *Measured the force required to separate the plates.*

**Adhesion to Si Wafer (lbf)**

| | Dried for 24h at RT | Dried for 24h at RT and 15h at 120°C in vacuum |
|---|---|---|
| PPy | 1.56 +/- 0.13 | 1.46 +/- 0.11 |
| PVdF | 1.63 +/- 0.05 | 0.043 +/- 0.016 |
| PAALi | VS adhesion | No adhesion |

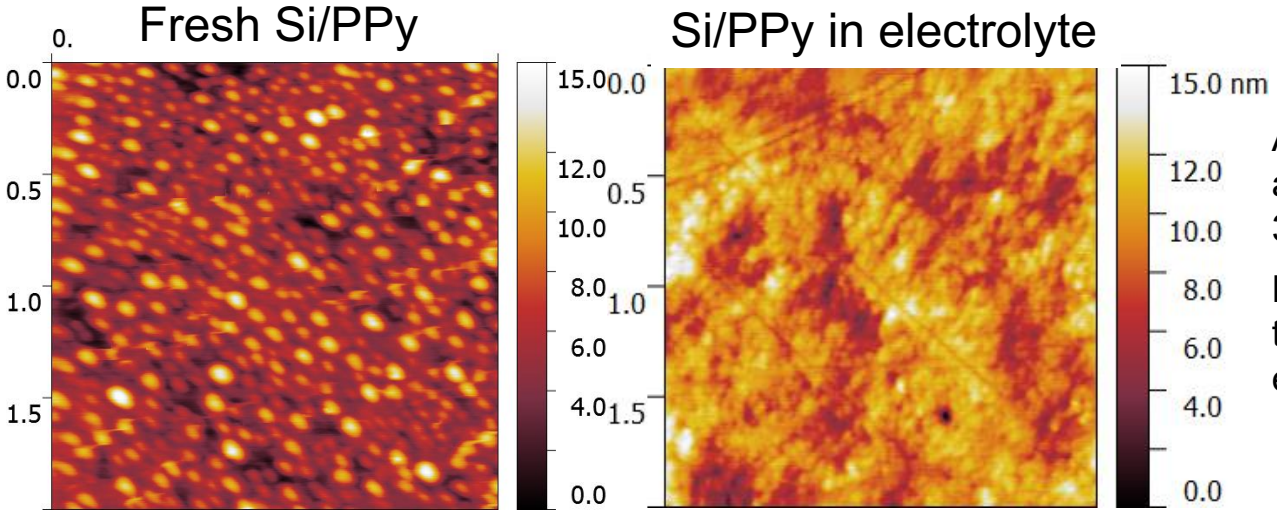
**Adhesion to Si/Cu Plate (lbf)**

| | Dried for 24h at RT | Dried for 24h at RT and 15h at 120°C in vacuum |
|---|---|---|
| PPy | Strong adhesion | Strong adhesion |
| PVdF | No adhesion | Strong adhesion |
| PAALi | 1.96 +/- 0.04 | Very strong adhesion |

- PPy adheres strongly to Si and Cu after drying at RT and/or at 120 °C.
- PAALi adheres strongly to Si and Cu after drying at RT. Adhesion to Si is lost after drying at 120 °C.
- PVdF adhesion to Si weakens after drying at 120°C. PVdF shows no adhesion to Cu after drying at RT and but it adheres very strongly to Cu after drying at 120°C.

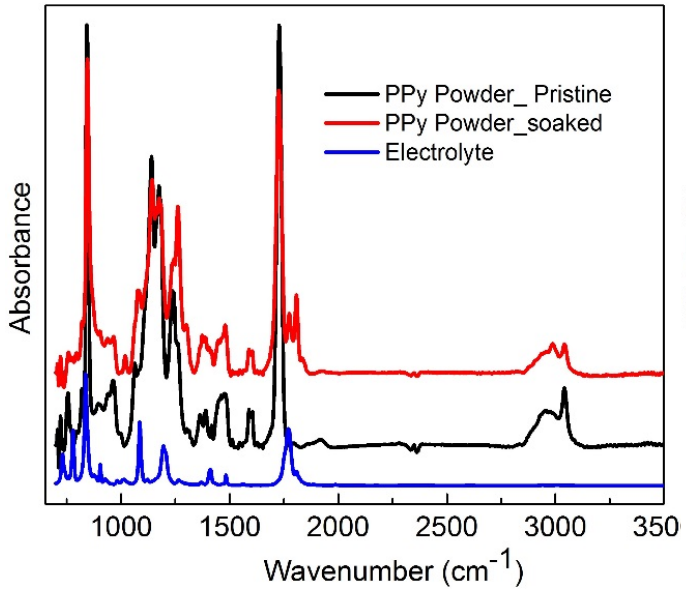
Binders adhesion and mechanical strength varies strongly with the type of material and processing conditions.

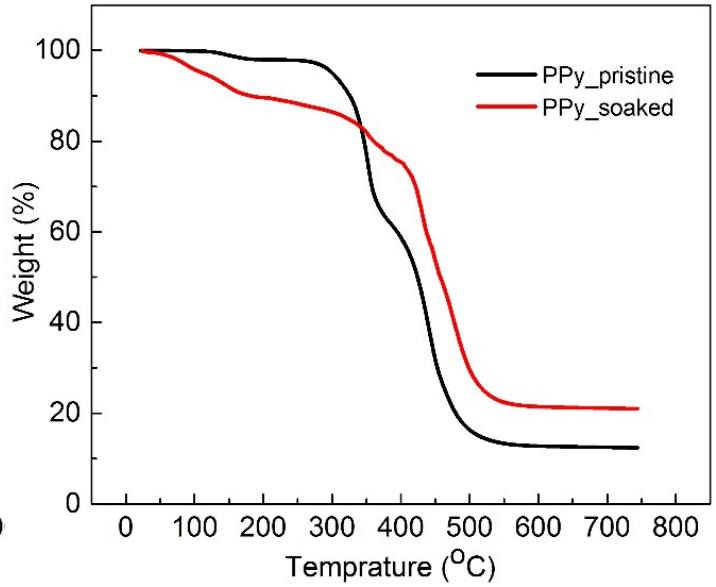
# PPy Chemical Stability vs. Electrolyte




AFM images of Si/PPy film before and after soaking the electrode for 30 min.

PPy morphology changes and film thickness increases due to the electrolyte intake.

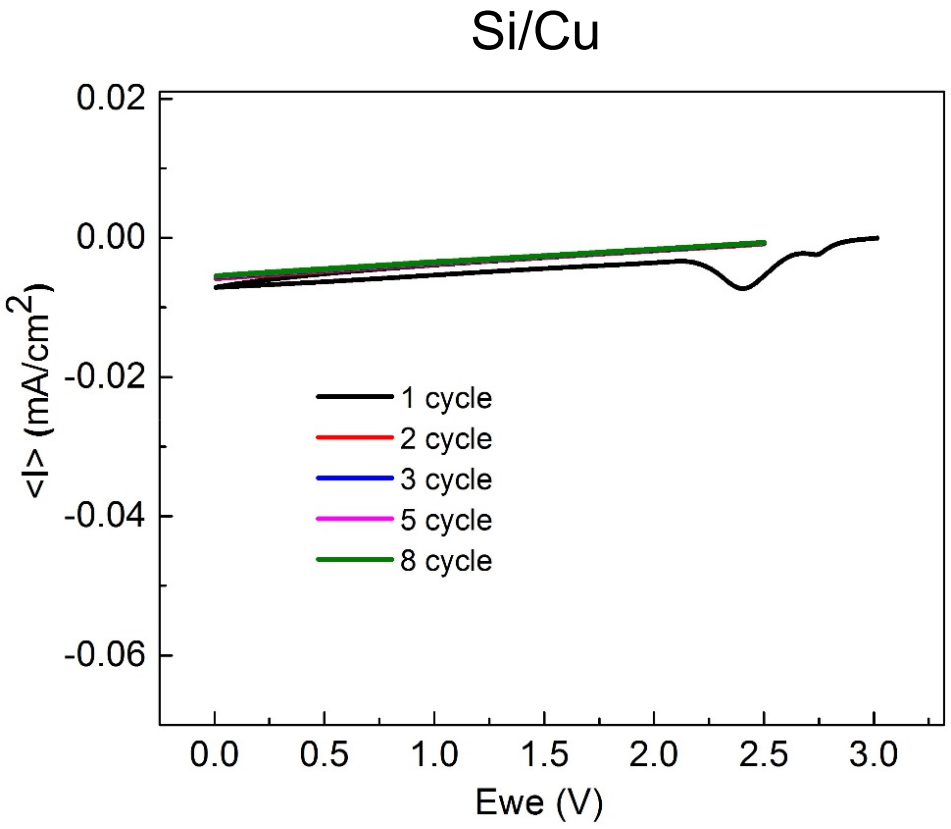


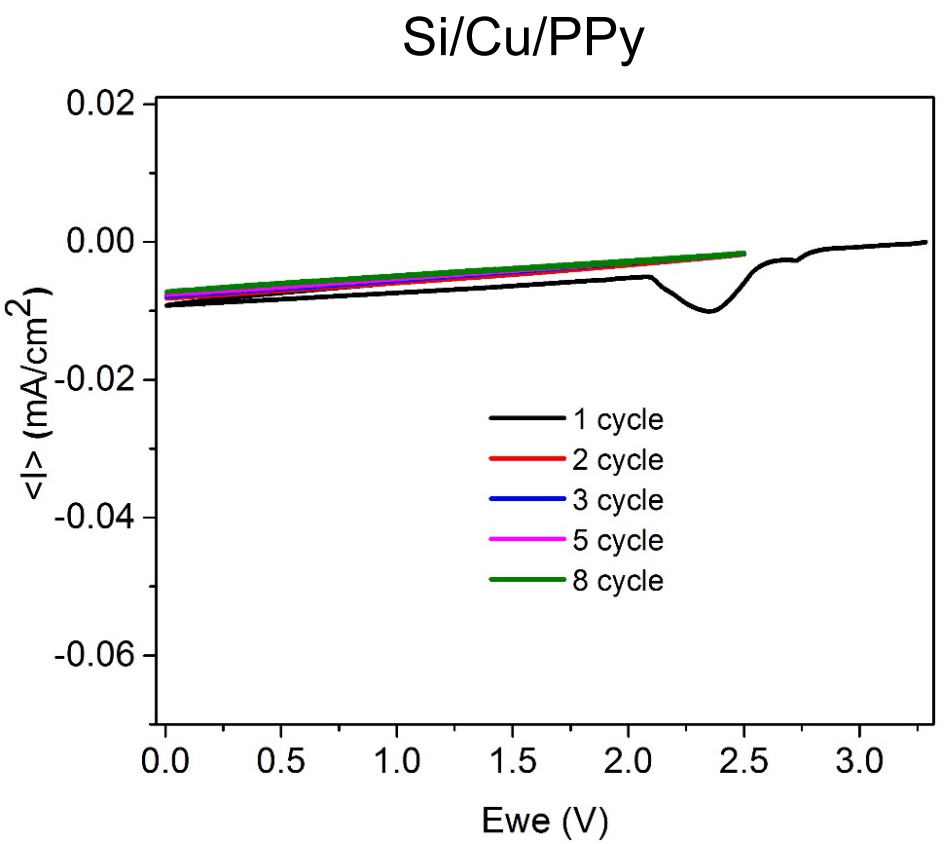




PPy powder was soaked for 24 h in the electrolyte, filtered and washed with DEC, dried for 24h in the glove box.

- FTIR spectra confirmed chemical stability of PPy in the electrolyte.
- FTIR peaks at 1775 and 1810 $cm^{-1}$ and TGA scans reveal DEC trapped in PPy.

# Cyclic Voltammetry of Cu and Cu/PPy Model Electrodes



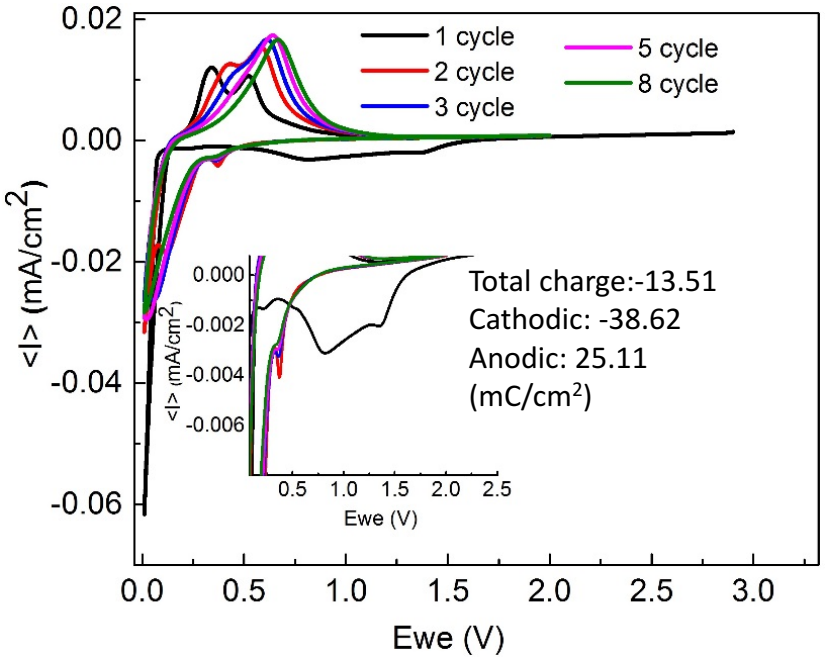




- CVs of Si/Cu/PPy showed similar features with that of Si/Cu electrode.
  - Cathodic current peak at 2.3 V corresponds to reduction of residual $CuO_x$.
  - No cathodic current due to the decomposition of the electrolyte or PPy.

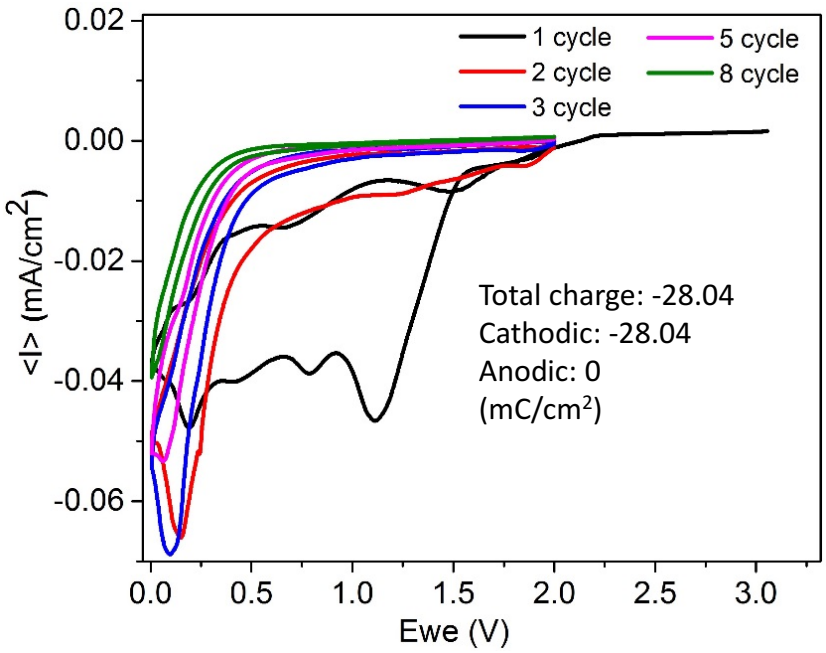
PPy is electrochemically stable within the Si anode cycling potential range

# Cyclic Voltammetry of Si and Si/PPy Model Electrodes

Pristine Si



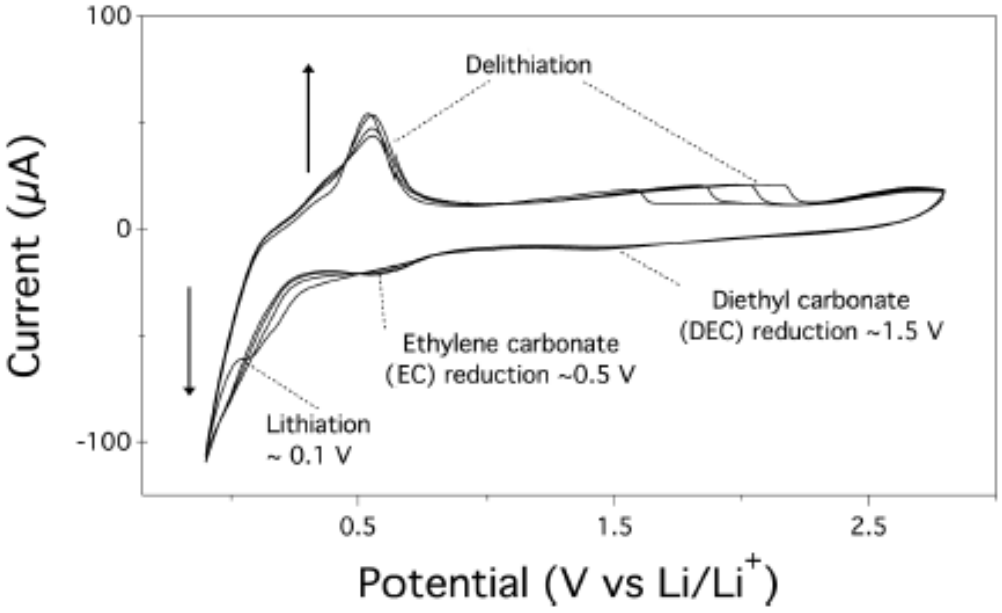

Si/PPy



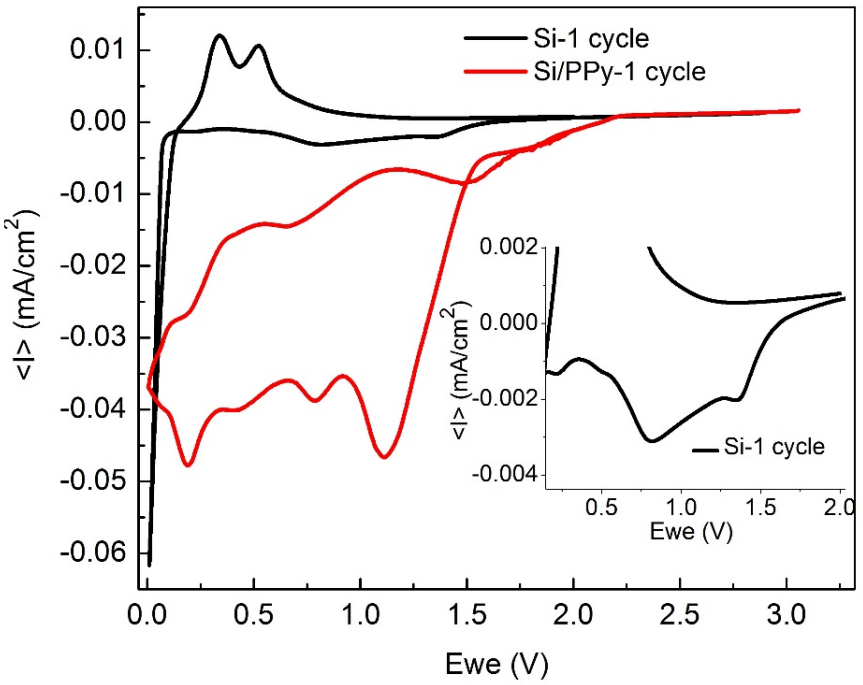

- Overall cathodic charge consumed during the first CV scan is higher for Si/PPy than Si.
- The charge consumed in cathodic process(es) is three orders of magnitude higher than the charge needed for complete decomposition of PPy to carbon (*Wilkes et al, JES, 2016, 163(3), A364)*
- Cathodic current peaks for Si/PPy are shifted toward lower potentials.
- Si surface passivates sooner than Si/PPy. No sign of lithiation of the underlying Si in Si/PPy after 8 cycles.

Si/PPy electrode shows excessive irreversible charge loss during initial CV cycles.

# Cyclic Voltammetry of Si and Si/PPy Model Electrodes

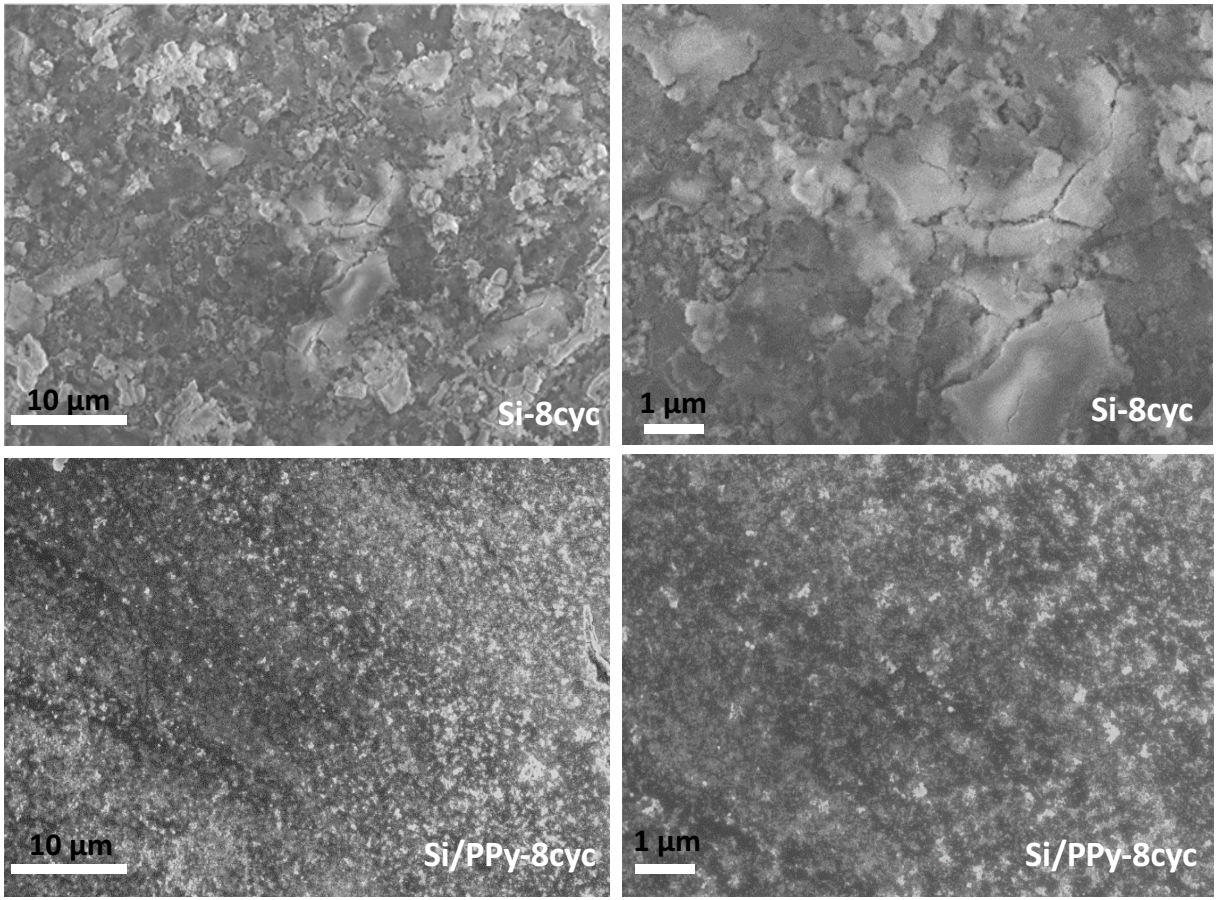



*Somorjai et al., J. Am. Chem. Soc. 2016, 138, 726−729



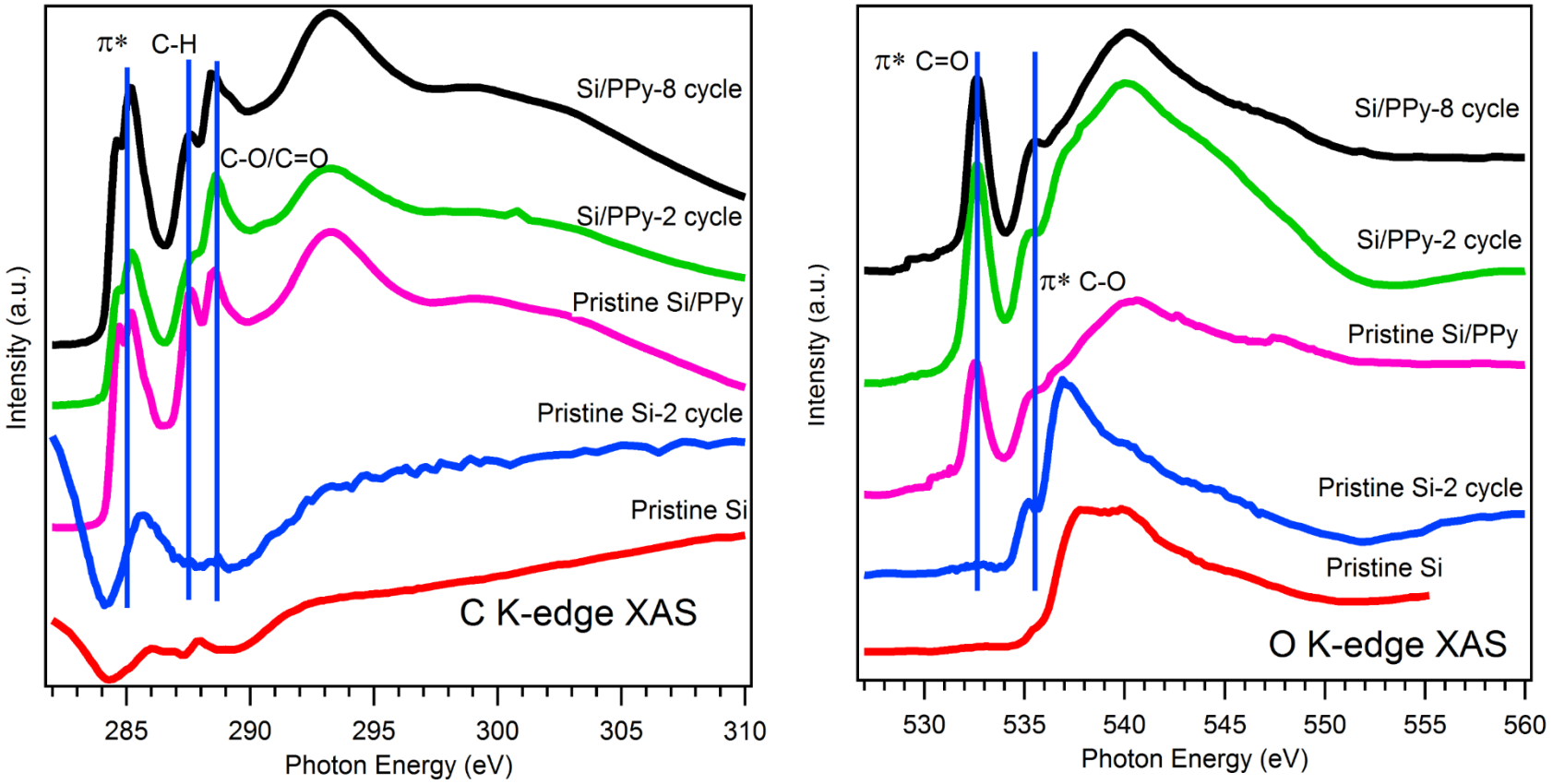

- Linear carbonates are reduced at higher potentials followed by the reduction of cyclic carbonates.*
- The electrolyte reduction current on Si/PPy is much higher than on Si electrode.
- PPy film changes Si interfacial reactivity by selective intake of DEC from the electrolyte.
  - Reduction of DEC produces soluble products. This leads to continuous decomposition of the electrolyte and non-passivating behavior.
- Solvated $Li^+$ ions are not allowed through the PPy film to reach Si surface.

# SEM of Cycled Si and Si/PPy Model Electrodes



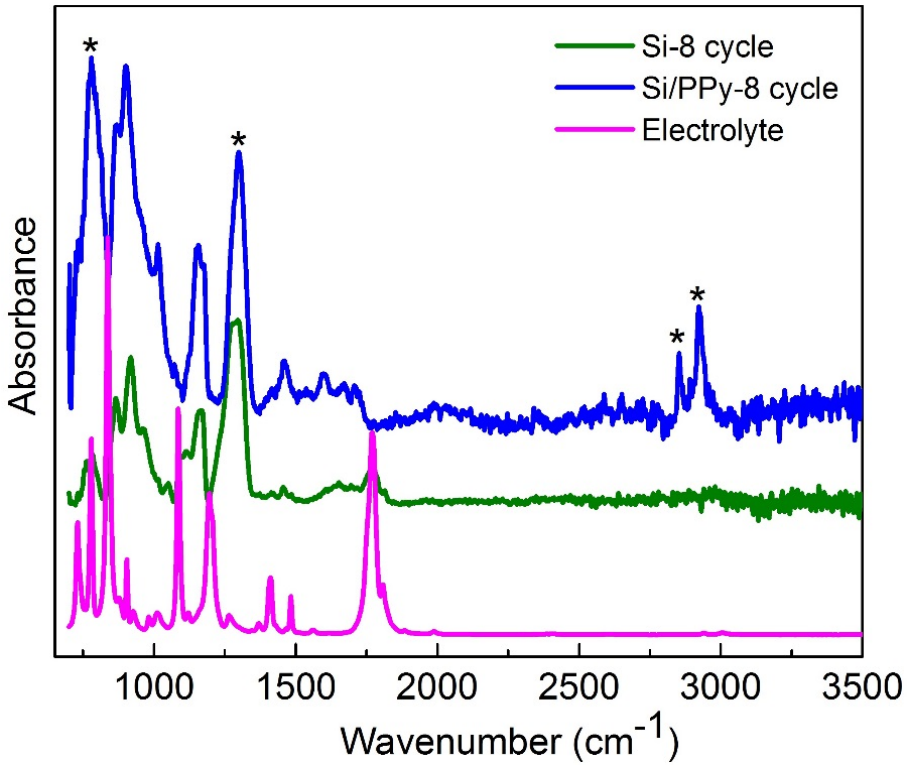

Large differences in surface morphology of cycled electrodes point at possible variations of the SEI formation/composition on Si and Si/PPy electrodes.

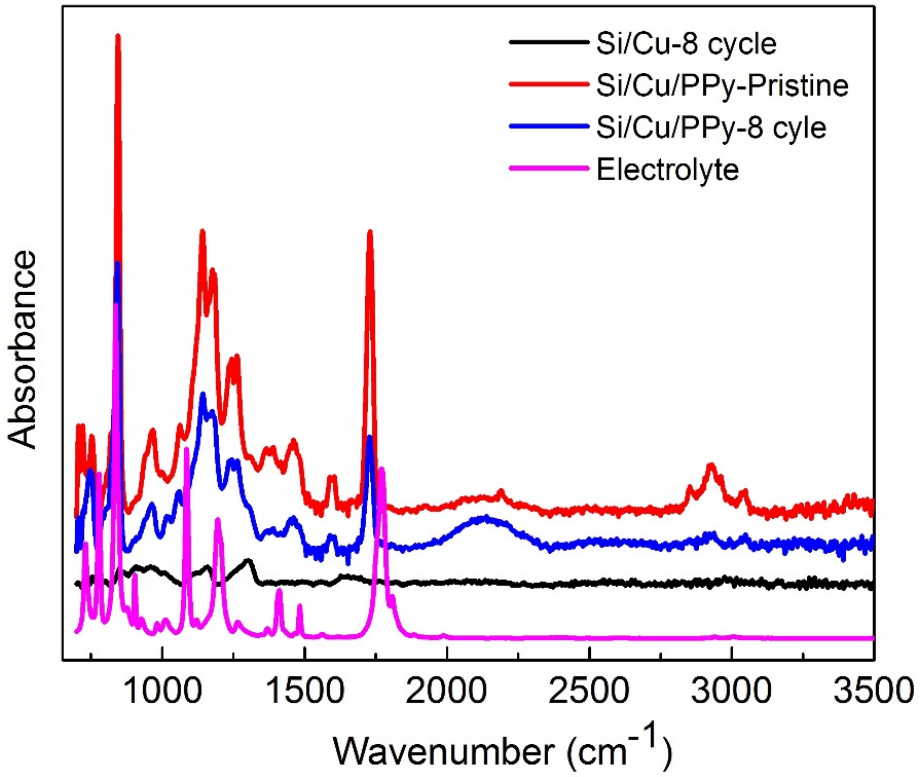
# *Ex situ* XAS of Si and Si/PPy Model Electrodes




- Typical π* features of C=C, C-O and C=O bonds of PPy are still clearly observed after 8 cycles.
- O K-edge spectra suggest different SEI products on Si and Si/PPy electrodes.

# *Ex situ* FTIR-ATR Studies of Model Electrodes

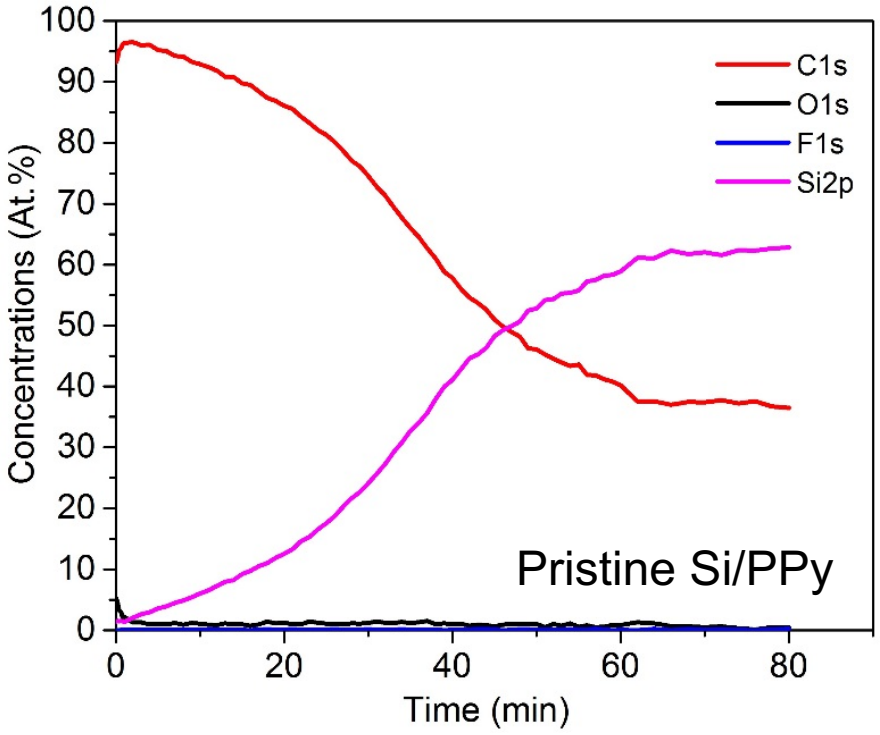


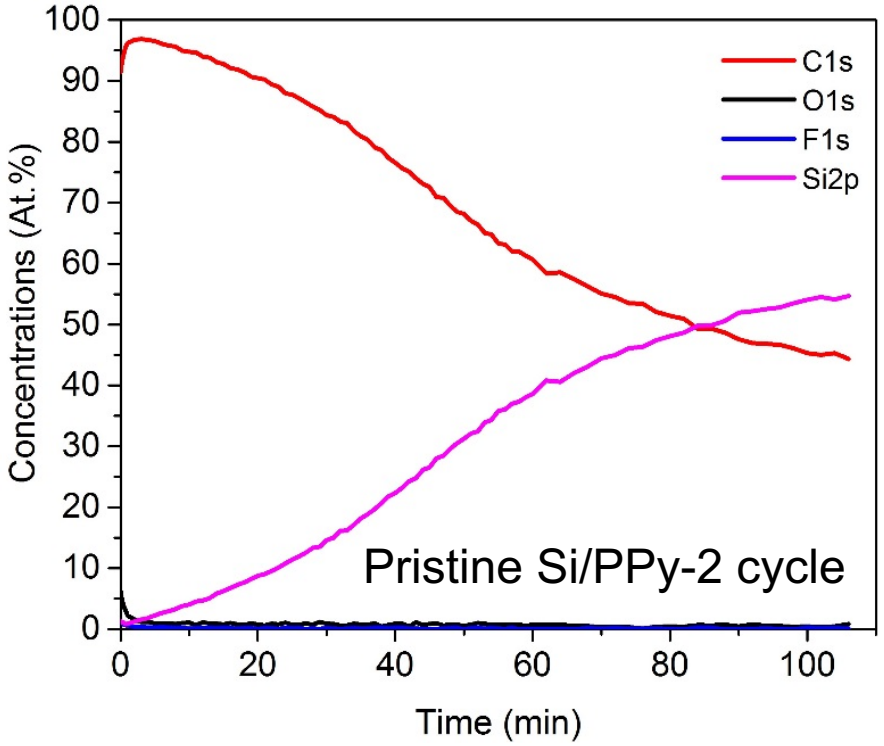




- PPy spectral characteristics are still observed after 8 cycles.
- FTIR spectra of cycled Si/PPy electrodes reveal tetramethoxy silane* trapped in the PPy film. Tetramethoxy silane can form in the reaction of alkyl radical intermediates with silicon oxide.
- The absence of tetramethoxy silane on Si electrode indicates that it gets dissolved in the electrolyte or washed away during the sample preparation process.

*Somorjai et al., J. Am. Chem. Soc. 2016, 138, 726−729*
*Michalak et al., Nat. Mater. 2010, 9, 266 and J. Phys. Chem. C 2008, 112, 11907.*

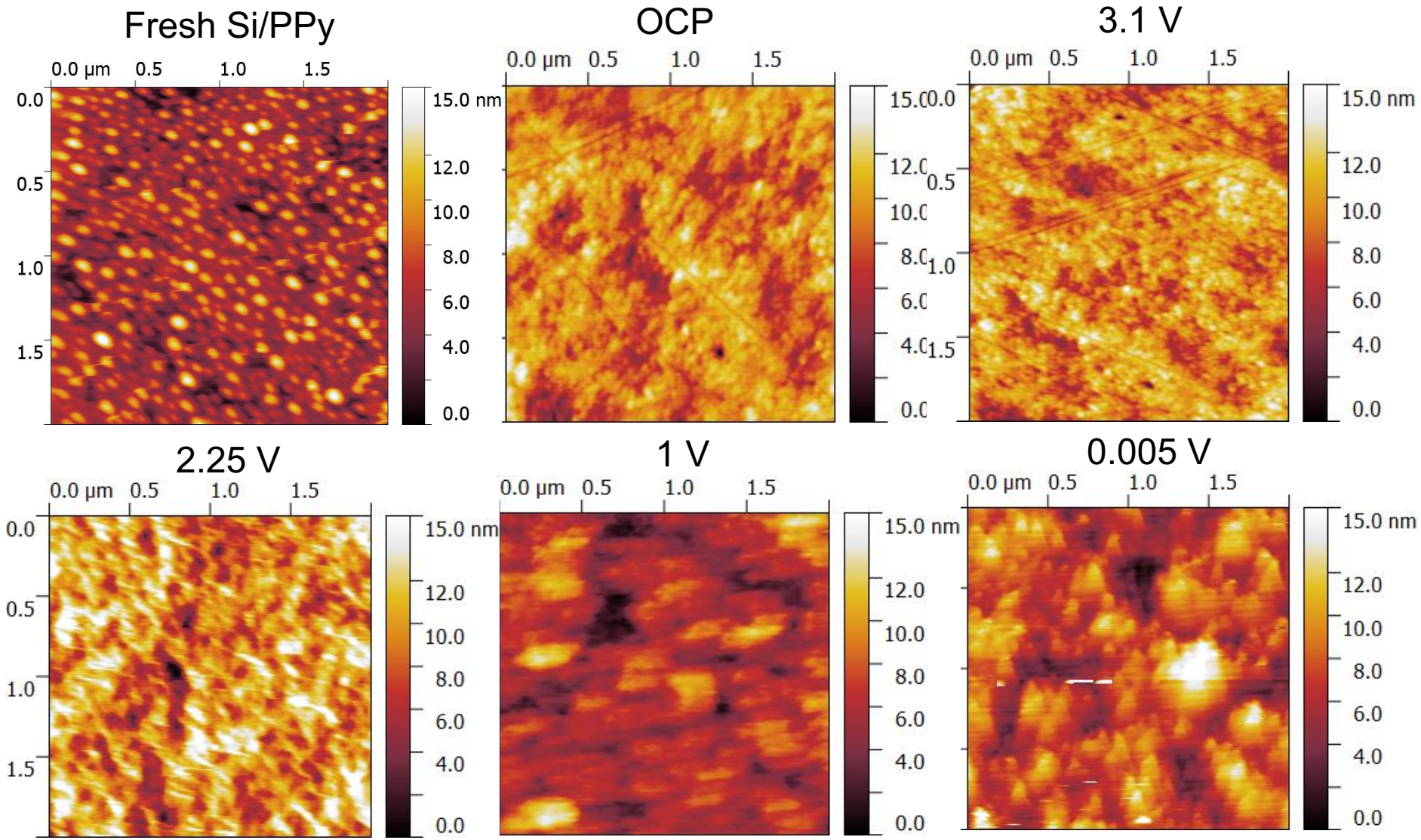
# *Ex situ* XPS Depth Profiling of Si/PPy Model Electrodes




The increased amount of carbon at the surface of Si/PPy electrode after 2 cycles originates from the electrolyte trapped in PPy and/or electrolyte decomposition products.

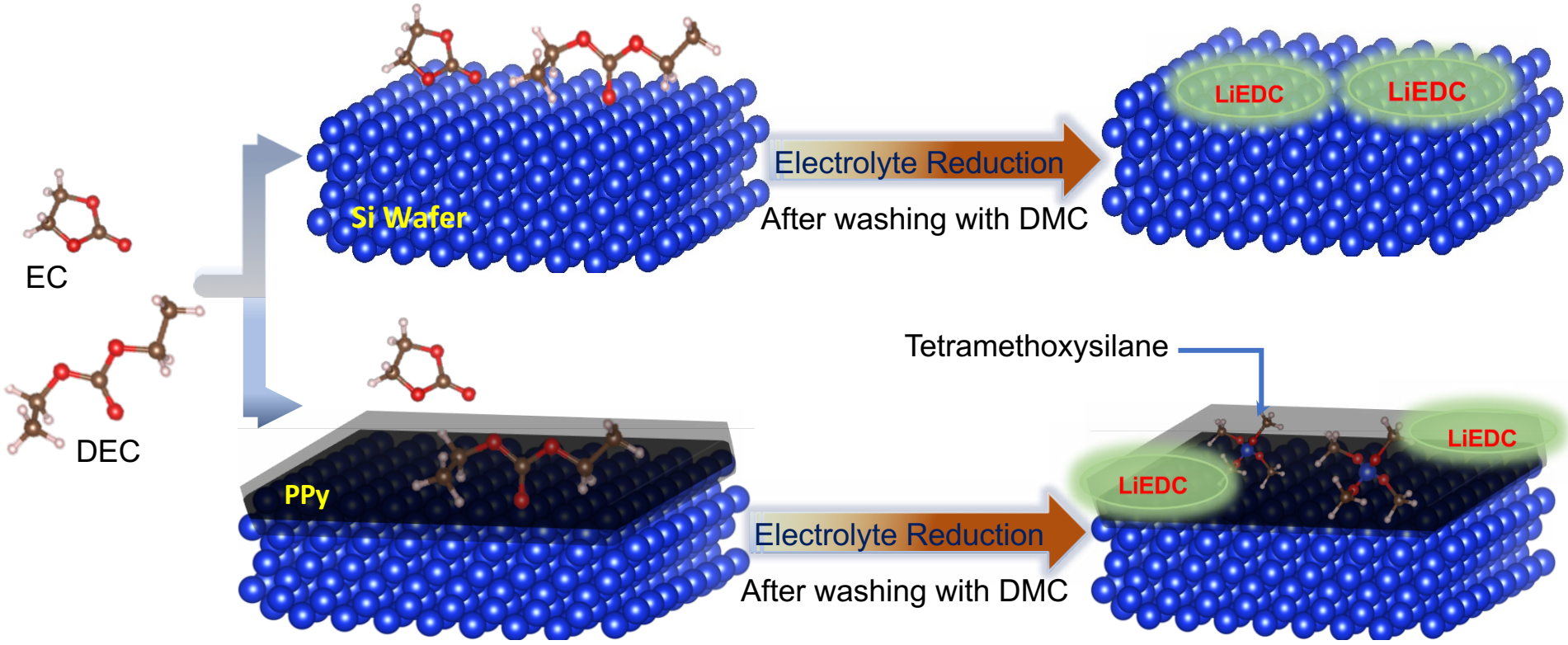
# *In situ* AFM Imaging of Si/PPy Model Electrodes




Variations of surface morphology corresponds to PPy swelling and SEI layer formation

# Surface Reactivity of Si and Si/PPy Model Electrodes

## Electrolyte Reduction Mechanism




PPy preferentially absorbs DEC. DEC reduction intermediates react with native $SiO_2$ to form tetramethoxy silane which gets trapped in the PPy film. Other soluble DEC reduction products diffuse into the electrolyte.

*Somorjai et al., J. Am. Chem. Soc. 2016, 138, 726* *Michalak et al., Nat. Mater. 2010, 9, 266 and J. Phys. Chem. C 2008, 112, 11907.*

# Summary

1. Cyclic voltammetry, X-ray absorption, Fourier transform infrared spectroscopy, XPS depth profiling and thermo-gravimetric analysis confirmed that the PPy binder is chemically stable during cycling of the Si electrode.

2. PPy shows superior adhesion to Si and Cu surface. It can improve mechanical integrity and stability of Si composite electrodes.

    - Effective binders should exhibit good adhesion and mechanical properties toward electrode active and passive components.

3. PPy film alteres the interfacial chemistry of silicon electrode by selective transport of electrolyte components and electrolyte decomposition products.

    - Binders can alter greatly interfacial reactivity, and their molecular structure as well as electrode preparation should be tailored carefully for this functions.

*This study not only determines the mechanism of PPy interactions in composite Si electrodes but also offer unique insights into rational design principles of advanced multifunctional binders for intermetallic Li-ion anodes.*

# Remaining Challenges and Barriers

1. Inherent non-passivating behavior of intermetallic Li-ion anode materials in organic electrolytes
   - Large irreversible capacity loss
   - Gradual electrolyte consumption and lithium inventory shift
2. Large volume changes during lithiation/delithiation cycling
   - Cracking and decrepitation exposing fresh surface to electroyte
   - Loss of electronic inter-connectivity and mechanical integrity

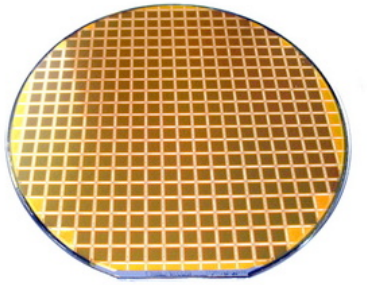
*Approach: Design and deploy model electrodes and unique analytical setup to probe and understand the function and operation of IM/electrolyte (IM= Si, Ge, Sn, Sb etc.) interfaces and interphases.*

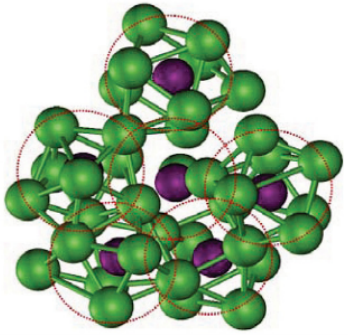
# Future Work: Three Themes for Research with Staggered Timelines

Any proposed future work is subject to change based on funding levels

## I. Use Model Electrodes for Control and Modification of Physico-Chemical Properties

- Probe and characterize electrode surface reactivity, composition and structure of the SEI layer at the basic building blocks level.
- Unveil hidden previously undetected SEI layer components.
- Ab-initio molecular dynamics simulation of (semi-) metallic glasses.





**Model Electrodes:**

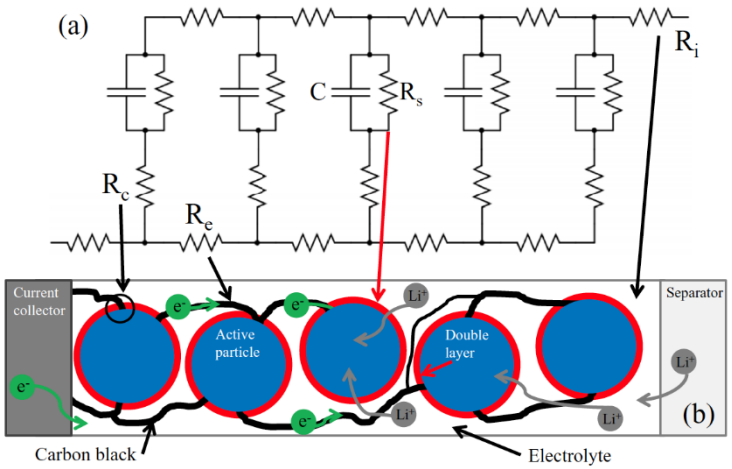
1. Si(100) wafers p-type (boron-doped)
2. Si amorphous thin films
3. Amorphous metals and alloys made by splat-quenching

# Future Work: Three Themes for Research with Staggered Timelines

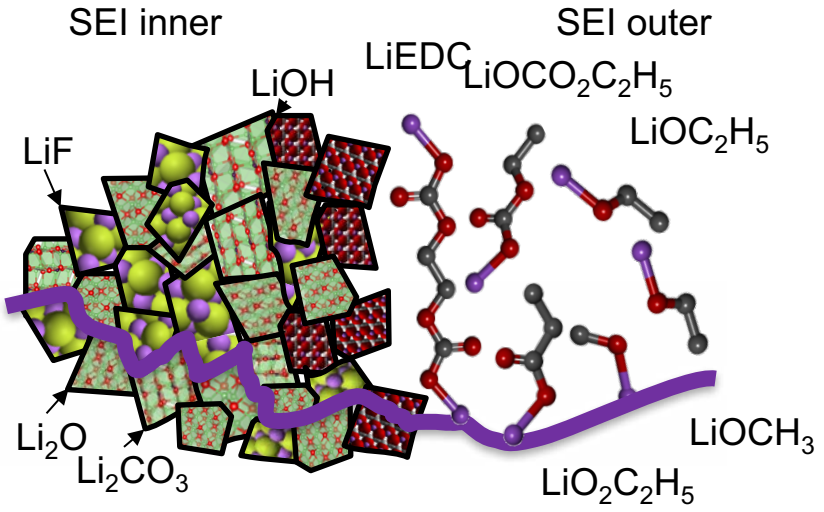
Any proposed future work is subject to change based on funding levels

## II. Correlation of Interfacial Properties with Electrochemical Behavior and Electrode Performance Challenges.

- Formulate working hypothesis of the mass and charge transfer across the surface film.
- Develop methods to track $Li^+$ in the film and electrode active material.
- Use and investigate chemical spillover effects e.g., SEI poisoning, local effects of graphite, binder etc.




Abarbanel et al., *J. Electrochem. Soc.* 2016,163, A522

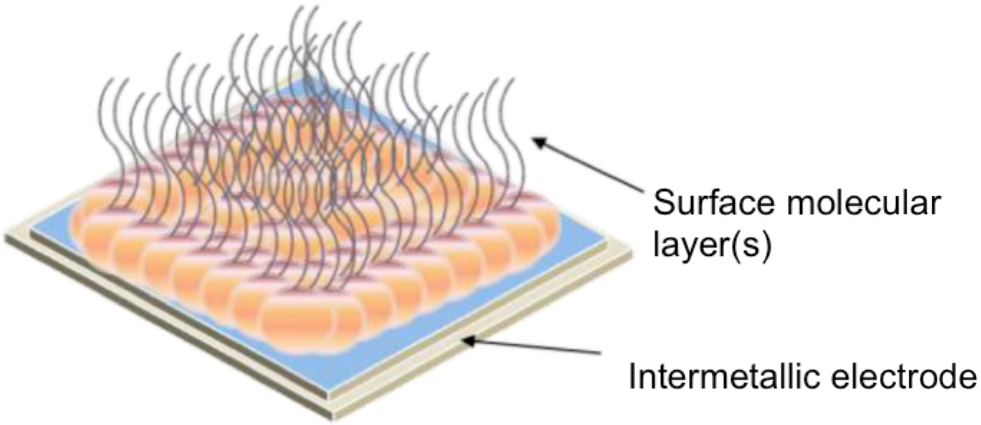


# Future Work: Three Themes for Research with Staggered Timelines

Any proposed future work is subject to change based on funding levels

## III. Modifications to Model Electrodes that Successfully Address Performance Challenges

- Correlate modifications to specific challenges, e.g. surface reactivity to electrolyte, volume change, "cracking, etc.
- Design and study model electrodes with tailored interfaces to control the kinetics i.e., rate and selectivity of interfacial processes.




**Modifications:**

1. Coatings of varying thickness oxidation, ALD and CVD
2. Alloys of varying combinations mostly of the elements Al, Si, Ge, In, Sn and Sb with P and B doping to enhance amorphous phase formation.